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First-order nonadiabatic couplings in extended systems by time-dependent density functional theory

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We propose an *ab initio* formulation that enables a *rigorous* calculation of the first-order nonadiabatic couplings (NAC) between electronic states based on time-dependent density functional theory in conjunction with planewave bases, projector augmented-wave pseudopotentials, and hybrid exchange-correlation functionals. The linear and quadratic time-dependent response theory is used to derive analytic expressions for the NAC matrix elements. In contrast to the previous formulation in atomic basis sets, the present formulation eliminates explicit references to Kohn-Sham virtual orbitals. With the introduction of Lagrangian functionals, the present formulation circumvents expensive derivative calculations of Kohn-Sham orbitals with respect to ionic coordinates. As a validation of the formulation, the NAC matrix elements of small molecules LiH and HeH^+ are calculated and compared to previous results with the atomic orbital basis. This development paves the way for accurate *ab initio* nonadiabatic molecular dynamics in extended systems. *Published by AIP Publishing.*
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I. INTRODUCTION

Nonadiabatic (NA) electron-ion coupling dynamics are ubiquitous and essential to many important problems in physics, chemistry, and materials science, ranging from interfacial charge transfer, formation of polarons, charge transport, exciton diffusion and dynamics, photocatalysis, and chemical reactions to name a few.[1–4] The first-order NA couplings (NAC) between two electronic states are crucial quantities that control the NA dynamics. For instance, they determine the probabilities of nonadiabatic transitions among potential energy surfaces (PESs) and the velocity adjustment. The latter plays a critical role to yield a long-term Boltzmann distribution and detailed balance for the electronic states.[5–7] In addition, NAC are key ingredients which account for electron (exciton)-phonon coupling strengths in materials. Nowadays, time-dependent density functional theory (TDDFT)[8,9] has become one of the most powerful, versatile, and popular tools to probe electronic structure and excitations in molecular and solid-state materials.[10–13] However, the evaluation of NAC via TDDFT has been an enduring challenge due to the fact that the many-body wavefunctions of the ground and excited states are inaccessible in TDDFT.[14] As a result, many approximate methods have been proposed to account for the NAC between a ground state and an excited state[15–20] and between two excited states[21–25] via TDDFT. It is only very recently that *exact* theories have been formulated by Send and Furche[26] to compute the ground state-excited state NAC and by Li *et al.* first[27,28] and Ou *et al.* subsequently[29] to compute the excited state-excited state NAC via TDDFT in atomic bases. More specifically, the NAC between the ground and excited states and between two excited states can be determined from the linear and the quadratic response theory, respectively, in TDDFT without the knowledge of the many-body wavefunctions. In the remainder of the paper, these exact theories will be referred to as NAC-TDDFT.

The previous NAC-TDDFT was formulated based on atomic orbitals (AO),[26–29] targeted primarily at molecular systems. The most important advantage of the AO bases is that hybrid functionals, crucial for TDDFT calculations, can readily be used even for large systems, while they are often quite expensive with planewave basis. However, many problems in chemical and materials research involve extended systems, such as 2D materials and their heterostructures, quantum and topological materials, halide perovskites, extended catalytic surfaces, and hybrid structures combining extended and finite systems, which are of tremendous current interest. Planewave bases are a natural choice for periodic and extended systems, offering advantages of simplicity, completeness, possibility of using Fast Fourier Transform algorithm, and absence of Pulay forces. Owing to these advantages, it is of great interest to reformulate the NAC-TDDFT so that it is applicable to plane waves and pseudopotentials.

Pseudopotentials are routinely used in conjunction with plane waves. Compared to ultrasoft[30] and norm-conserving[31,32] pseudopotentials, the projector augmented-wave (PAW)[33,34] pseudopotential has two advantages that are important to our objective: (1) Via a linear transformation, the pseudo-wavefunctions can be readily transformed to the true "all-electron (AE)" wavefunctions, which are key ingredients in the present formulation. (2) The PAW provides a higher transferability and a lower energy cutoff than the norm-conserving pseudopotentials. Here, we will focus on PAW in our formulation.

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The objective of this work is to reformulate NAC-TDDFT so that it can be used in conjunction of plane waves and PAW. The theoretical framework underlying the present deviations is the same as that in the AO based NAC-TDDFT,[26–29] i.e., the linear and quadratic time-dependent response theory of TDDFT. However, the explicit expressions of NAC are quite different from those in the AO based NAC-TDDFT. Moreover, the present formulation does not involve virtual Kohn-Sham (KS) orbitals, in contrast to the AO based NAC-TDDFT. In addition, the present formulation makes use of appropriate Lagrangians proposed previously[26–29] to enable efficient calculations of NAC. In Sec. II, we present the theoretical formulation based on plane waves and PAW. In Sec. III, the relevant NAC of small molecules LiH and HeH^+ are calculated using the formulation and compared to the previous results obtained by the AO based NAC-TDDFT. Finally, we conclude with an outlook for future development in Sec. IV.

II. METHODOLOGY

The basic idea of deducing NAC from the time-dependent response theory is to find the poles (residues) of the response function for the expectation value of a time-independent operator d/dx, when the system is perturbed by a time-dependent external potential. Here x denotes the ionic coordinate. Following Refs. 27 and 28, we define an auxiliary coupling which is the expectation value of d/dx. One can calculate the auxiliary coupling from both the exact many-body wavefunction based time-dependent perturbation theory and TDDFT. By comparing the residues of the auxiliary coupling thus obtained, one can extract the explicit formulation of NAC in the framework of TDDFT. Here, we only consider the Γ-point in the Brillouin zone, where the KS orbitals are taken to be real. In the following, we use indices $i, j, k, \ldots$ to label occupied KS orbitals, $\sigma, \tau, \ldots$ to denote their spins, $\alpha, \beta, \ldots$ to label excited states, and $\bar{a}, \bar{b}, \ldots$ to label the harmonic perturbing potential.

A. Many-body wavefunction based time-dependent perturbation theory

Considering a many-electron system, the energy and many-body wavefunction can be obtained by the eigenvalue equation of time-independent many-body Hamiltonian,

$$\hat{H}_0|\Psi_\alpha\rangle = E_\alpha|\Psi_\alpha\rangle. \tag{1}$$

The system initially stays on the ground state $\alpha = 0$. Starting from time $t = 0$, the system is perturbed by a harmonic perturbing potential with frequencies $\{\omega_{\bar{a}}\}$,

$$\delta\hat{V}_{\text{ext}}(t) = \sum_{\bar{a}}\left[\hat{V}^+_{\bar{a}}e^{i\omega_{\bar{a}}t} + \hat{V}^-_{\bar{a}}e^{-i\omega_{\bar{a}}t}\right]. \tag{2}$$

Since the external potential is real, we have $\hat{V}^+_{\bar{a}} = \left(\hat{V}^-_{\bar{a}}\right)^*$. The evolution of the many-body wavefunction follows the Schrodinger equation,

$$i\frac{\partial|\Psi(t)\rangle}{\partial t} = \left(\hat{H}_0 + \delta\hat{V}_{\text{ext}}(t)\right)|\Psi(t)\rangle. \tag{3}$$

Here, $|\Psi(t)\rangle$ is the exact time-dependent many-body wavefunction which can be expressed perturbatively up to the second order as

$$|\Psi(t)\rangle = e^{-iE_0t}\left(|\Psi_0\rangle + \left|\Psi^{(1)}(t)\right\rangle + \left|\Psi^{(2)}(t)\right\rangle\right), \tag{4}$$

where the first- and second-order many-body wavefunctions can be expressed by a linear combination of eigenstates of $\hat{H}_0$ as

$$\begin{aligned}\left|\Psi^{(1)}(t)\right\rangle &= \sum_\alpha B^{(1)}_\alpha(t)|\Psi_\alpha\rangle,\\ \left|\Psi^{(2)}(t)\right\rangle &= \sum_\alpha B^{(2)}_\alpha(t)|\Psi_\alpha\rangle.\end{aligned} \tag{5}$$

Substituting Eqs. (4) and (5) into the Schrodinger equation (3) and using the harmonic potential in Eq. (2), one can obtain the first- and second-order coefficients as

$$B^{(1)}_\alpha(t) = -\sum_{\bar{a}}\frac{\langle\Psi_\alpha|\hat{V}^+_{\bar{a}}|\Psi_0\rangle}{\omega_\alpha + \omega_{\bar{a}}}e^{i\omega_{\bar{a}}t} - \sum_{\bar{a}}\frac{\langle\Psi_\alpha|\hat{V}^-_{\bar{a}}|\Psi_0\rangle}{\omega_\alpha - \omega_{\bar{a}}}e^{-i\omega_{\bar{a}}t} \tag{6}$$

and

$$\begin{aligned}B^{(2)}_\alpha(t) = \sum_{\bar{a}\bar{b},\beta}\Bigg\{&\frac{\left\langle\Psi_\alpha\left|\hat{V}^+_{\bar{a}}\right|\Psi_\beta\right\rangle\left\langle\Psi_\beta\left|\hat{V}^+_{\bar{b}}\right|\Psi_0\right\rangle}{\left(\omega_\alpha + \omega_{\bar{a}} + \omega_{\bar{b}}\right)\left(\omega_\beta + \omega_{\bar{b}}\right)}e^{i(\omega_{\bar{a}}+\omega_{\bar{b}})t}\\ &+\frac{\left\langle\Psi_\alpha\left|\hat{V}^+_{\bar{a}}\right|\Psi_\beta\right\rangle\left\langle\Psi_\beta\left|\hat{V}^-_{\bar{b}}\right|\Psi_0\right\rangle}{\left(\omega_\alpha + \omega_{\bar{a}} - \omega_{\bar{b}}\right)\left(\omega_\beta - \omega_{\bar{b}}\right)}e^{i(\omega_{\bar{a}}-\omega_{\bar{b}})t}\\ &+\frac{\left\langle\Psi_\alpha\left|\hat{V}^-_{\bar{a}}\right|\Psi_\beta\right\rangle\left\langle\Psi_\beta\left|\hat{V}^+_{\bar{b}}\right|\Psi_0\right\rangle}{\left(\omega_\alpha - \omega_{\bar{a}} + \omega_{\bar{b}}\right)\left(\omega_\beta + \omega_{\bar{b}}\right)}e^{i(-\omega_{\bar{a}}+\omega_{\bar{b}})t}\\ &+\frac{\left\langle\Psi_\alpha\left|\hat{V}^-_{\bar{a}}\right|\Psi_\beta\right\rangle\left\langle\Psi_\beta\left|\hat{V}^-_{\bar{b}}\right|\Psi_0\right\rangle}{\left(\omega_\alpha - \omega_{\bar{a}} - \omega_{\bar{b}}\right)\left(\omega_\beta - \omega_{\bar{b}}\right)}e^{i(-\omega_{\bar{a}}-\omega_{\bar{b}})t}\Bigg\},\end{aligned} \tag{7}$$

where $\omega_\alpha = E_\alpha - E_0$ is the αth excitation energy.

The auxiliary coupling $C(t)$ based on the time-dependent many-body wavefunction is defined as

$$C(t) = \left\langle\Psi(t)\left|\frac{d}{dx}\right|\Psi(t)\right\rangle. \tag{8}$$

We first consider the first-order auxiliary coupling $C^{(1)}(t)$. Substituting Eq. (4) into Eq. (8) and collecting the coefficients of $e^{i\omega_{\bar{a}}t}$, one can find the residue of $C^{(1)}(t)$ at frequency ω_α as

$$\lim_{\omega_{\bar{a}}\to\omega_\alpha}(\omega_\alpha - \omega_{\bar{a}})C^{(1)}(\omega_{\bar{a}}) = \left\langle\Psi_0\left|\hat{V}^+_{\bar{a}}\right|\Psi_\alpha\right\rangle\left\langle\Psi_0\left|\frac{d}{dx}\right|\Psi_\alpha\right\rangle. \tag{9}$$

Clearly, the second bracket at the right-hand side of Eq. (9) is NAC, $g^x_{0\alpha}$, between the ground state and the αth excited state. Similarly, for the second-order auxiliary coupling $C^{(2)}(t)$, substituting Eq. (4) into Eq. (8) and collecting the coefficients of $e^{i(\omega_{\bar{a}}+\omega_{\bar{b}})t}$, one can find the residue of $C^{(2)}(t)$ at frequencies $\omega_{\bar{a}} = \omega_\alpha$ and $\omega_{\bar{b}} = -\omega_\beta$ as

$$\begin{aligned}&\lim_{\omega_{\bar{a}}\to\omega_\alpha,\omega_{\bar{b}}\to-\omega_\beta}(\omega_\alpha - \omega_{\bar{a}})\left(\omega_\beta + \omega_{\bar{b}}\right)C^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}})\\ &\quad= \left\langle\Psi_0\left|\hat{V}^+_{\bar{a}}\right|\Psi_\alpha\right\rangle\left\langle\Psi_\beta\left|\hat{V}^+_{\bar{b}}\right|\Psi_0\right\rangle\left\langle\Psi_\alpha\left|\frac{d}{dx}\right|\Psi_\beta\right\rangle.\end{aligned} \tag{10}$$

The third bracket at the right-hand side of Eq. (10) is just NAC, $g^x_{\alpha\beta}$, between the αth and the βth excited states. The next step is to determine the residues of the auxiliary couplings based on TDDFT.

B. Brief summary of PAW method

In this subsection, we present the basic concepts of the PAW formalism, which are necessary to understand the PAW

implementation of first- and second-order TDKS equations and the NAC matrix. In the PAW method,[33,34] the all-electron (AE) wavefunction $|\psi_i\rangle$ is a linear transformation of the pseudo-wavefunction (PS) $|\tilde{\psi}_i\rangle$ as

$$|\psi_{i\sigma}\rangle = \mathcal{T}|\tilde{\psi}_{i\sigma}\rangle = |\tilde{\psi}_{i\sigma}\rangle + \sum_I \left(|\phi_I\rangle - |\tilde{\phi}_I\rangle\right)\langle\tilde{p}_I|\tilde{\psi}_{i\sigma}\rangle, \quad (11)$$

where ϕ_I, $\tilde{\phi}_I$, and $\tilde{p}_I$ are the AE partial waves, the PS partial waves, and the projector functions, respectively, defined in the core region. The index I also includes the angular momentum quantum numbers and an additional index for the reference energy. The AE charge density related to the orbitals i and j is calculated as

$$n_{ij\sigma}(r) = \psi^*_{i\sigma}(r)\psi_{j\sigma}(r) = \tilde{n}_{ij\sigma}(r) - \tilde{n}^1_{ij\sigma}(r) + n^1_{ij\sigma}(r), \quad (12)$$

where $\tilde{n}$ is the PS charge density calculated on a uniform plane-wave grid. $\tilde{n}^1$ and n^1 are one-center charge densities computed on a radial grid within the core region of each ion. To treat the long-range electrostatic interaction between the core charge density and the PS charge density, a compensation charge density $\hat{n}$ on the plane-wave grid is introduced as

$$\hat{n}_{ij\sigma}(r) = \sum_{IJ,LM} \langle\tilde{\psi}_{i\sigma}|\tilde{p}_I\rangle\langle\tilde{p}_J|\tilde{\psi}_{j\sigma}\rangle\hat{Q}^{LM}_{IJ}(r), \quad (13)$$

where the function $\hat{Q}^{LM}_{IJ}(r)$ can be found in Eq. (27) of Ref. 34. $\tilde{n}^1_{ij} + \hat{n}_{ij}$ has the same moments as the exact density $\tilde{n}^1_{ij}$ within the core. The action of KS Hamiltonian onto each orbital is given by[34,35]

$$\begin{aligned}\tilde{H}^\sigma|\tilde{\psi}_{i\sigma}\rangle = &\left(-\frac{1}{2}\nabla^2 + \tilde{V}^\sigma_{\rm loc}\right)|\tilde{\psi}_{i\sigma}\rangle + \sum_{IJ}|\tilde{p}_I\rangle\left(\hat{D}_{IJ}\left[\tilde{V}^\sigma_{\rm loc}\right] + D^1_{IJ} - \tilde{D}^1_{IJ}\right)\langle\tilde{p}_J|\tilde{\psi}_{i\sigma}\rangle - \sum_j \tilde{V}_{\rm EX}\left[\tilde{n}_{ji\sigma} + \hat{n}_{ji\sigma}\right]|\tilde{\psi}_{j\sigma}\rangle \\ &- \sum_{j,IJ}|\tilde{p}_I\rangle\hat{D}_{IJ}\left[\tilde{V}_{\rm EX}\right]\langle\tilde{p}_J|\tilde{\psi}_{j\sigma}\rangle - \sum_{(I,K)(J,L)}\left(K^1_{IJLK} - \tilde{K}^1_{IJLK}\right)\rho^\sigma_{LJ}|\tilde{p}_I\rangle\langle\tilde{p}_K|\tilde{\psi}_{i\sigma}\rangle, \end{aligned} \quad (14)$$

where $\tilde{V}^\sigma_{\rm loc}$ is the KS effective local potential consisting of Hartree, local exchange-correlation, and local pseudopotential terms, which is evaluated on the plane-wave grid. $\hat{D}_{IJ}\left[\tilde{V}\right] = \sum_{LM}\int\tilde{V}(r)\hat{Q}^{LM}_{IJ}(r)dr$. $\left(D^1_{IJ} - \tilde{D}^1_{IJ}\right)$ is calculated by $\partial\left(E^1 - \tilde{E}^1\right)/\partial\rho^\sigma_{IJ}$, where E^1 and $\tilde{E}^1$ are parts of the total energy computed on the radial grid[34] and $\rho^\sigma_{IJ} = \sum_i\langle\tilde{\psi}_{i\sigma}|\tilde{p}_I\rangle\langle\tilde{p}_J|\tilde{\psi}_{i\sigma}\rangle$ is the occupancy of each augmentation channel (I, J). $\tilde{V}_{\rm EX}$ is the two-orbital exchange potential and K^1_{IJLK} ($\tilde{K}^1_{IJLK}$) is the two-electron four-AE (PS)-partial-wave integral.[35] Here, the symbol EX represents a generalized exchange, which can include a long-range interaction operator, such as the error function $r^{-1}\mathrm{erf}(r)$. Thus, one can also exploit various hybrid functionals, such as PBE0,[36] range-separated hybrid (RSH) functional,[37,38] and optimally tuned RSH for solids.[39] The ground state KS equation is then expressed as

$$\tilde{H}^\sigma|\tilde{\psi}_{i\sigma}\rangle = \sum_j \epsilon_{ij\sigma}\tilde{S}|\tilde{\psi}_{j\sigma}\rangle, \quad (15)$$

with the orthonormal condition $\langle\tilde{\psi}_{i\sigma}|\tilde{S}|\tilde{\psi}_{j\tau}\rangle = \delta_{ij}\delta_{\sigma\tau}$, where $\tilde{S} = \mathcal{T}^\dagger\mathcal{T}$ is the overlap operator.

C. First- and second-order perturbation in TDDFT

Considering a system perturbed by an external potential, the TD-KS orbitals $|\tilde{\psi}(t)\rangle$ satisfy the TDKS equation,

$$i\tilde{S}\frac{d}{dt}|\tilde{\psi}_{i\sigma}(t)\rangle = \left[\tilde{H}^\sigma(t) + \delta\tilde{V}_{\rm ext}(t)\right]|\tilde{\psi}_{i\sigma}(t)\rangle, \quad (16)$$

where $\delta\tilde{V}_{\rm ext}$ is the external perturbing potential. The TD-KS orbitals also satisfy the orthonormal condition $\langle\tilde{\psi}_{i\sigma}(t)|\tilde{S}|\tilde{\psi}_{j\tau}(t)\rangle = \delta_{ij}\delta_{\sigma\tau}$. Up to the second-order perturbation, we can express the corresponding TD-KS orbital as

$$|\tilde{\psi}_{i\sigma}(t)\rangle = e^{-i\epsilon_{i\sigma}t}\left(|\tilde{\psi}_{i\sigma}\rangle + |\tilde{\psi}^{(1)}_{i\sigma}\rangle + |\tilde{\psi}^{(2)}_{i\sigma}\rangle\right). \quad (17)$$

Here, $|\tilde{\psi}_{i\sigma}\rangle$ refers to the time-independent ground-state KS orbital. $|\tilde{\psi}^{(1)}_{i\sigma}\rangle$ and $|\tilde{\psi}^{(2)}_{i\sigma}\rangle$ are the time-dependent first- and second-order TDKS orbitals. Substituting Eq. (17) into Eq. (16), we arrive at the first-order TDKS equation

$$\tilde{H}^\sigma|\tilde{\psi}^{(1)}_{i\sigma}\rangle + \sum_{j\tau}\langle\tilde{\psi}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}_{j\tau}\tilde{\psi}^{(1)}_{j\tau}\rangle + \sum_{j\tau}\langle\tilde{\psi}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}_{j\tau}\rangle + \delta\tilde{V}_{\rm ext}(t)|\tilde{\psi}_{i\sigma}\rangle = \epsilon_{i\sigma}\tilde{S}|\tilde{\psi}^{(1)}_{i\sigma}\rangle + i\tilde{S}\frac{d}{dt}|\tilde{\psi}^{(1)}_{i\sigma}\rangle \quad (18)$$

and the second-order TDKS equation

$$\begin{aligned}\tilde{H}^\sigma|\tilde{\psi}^{(2)}_{i\sigma}\rangle &+ \sum_{j\tau}\langle\tilde{\psi}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}_{j\tau}\tilde{\psi}^{(2)}_{j\tau}\rangle + \sum_{j\tau}\langle\tilde{\psi}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}^{(2)}_{j\tau}\tilde{\psi}_{j\tau}\rangle + \sum_{j\tau}\langle\tilde{\psi}^{(1)}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}_{j\tau}\tilde{\psi}^{(1)}_{j\tau}\rangle + \sum_{j\tau}\langle\tilde{\psi}^{(1)}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}_{j\tau}\rangle \\ &+ \sum_{j\tau}\langle\tilde{\psi}_{i\sigma}|\tilde{K}_{\sigma\tau}|\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}^{(1)}_{j\tau}\rangle + \frac{1}{2}\sum_{jj'\tau\tau'}\left[\langle\tilde{\psi}_{i\sigma}|\tilde{K}'_{\sigma\tau\tau'}|\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}_{j\tau}\tilde{\psi}^{(1)}_{j'\tau'},\tilde{\psi}_{j'\tau'}\rangle + \langle\tilde{\psi}_{i\sigma}|\tilde{K}'_{\sigma\tau\tau'}|\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}_{j\tau}\tilde{\psi}_{j'\tau'},\tilde{\psi}^{(1)}_{j'\tau'}\rangle\right. \\ &\left.+\langle\tilde{\psi}_{i\sigma}|\tilde{K}'_{\sigma\tau\tau'}|\tilde{\psi}_{j\tau}\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}^{(1)}_{j'\tau'},\tilde{\psi}_{j'\tau'}\rangle + \langle\tilde{\psi}_{i\sigma}|\tilde{K}'_{\sigma\tau\tau'}|\tilde{\psi}_{j\tau}\tilde{\psi}^{(1)}_{j\tau}\tilde{\psi}_{j'\tau'},\tilde{\psi}^{(1)}_{j'\tau'}\rangle\right] + \delta\tilde{V}_{\rm ext}(t)|\tilde{\psi}^{(1)}_{i\sigma}\rangle = \epsilon_{i\sigma}\tilde{S}|\tilde{\psi}^{(2)}_{i\sigma}\rangle + i\tilde{S}\frac{d}{dt}|\tilde{\psi}^{(2)}_{i\sigma}\rangle. \end{aligned} \quad (19)$$

Here, we have defined the orbitals via the kernel functional as

$$\begin{aligned}\left\langle\tilde{\psi}_{j\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{k\tau}\tilde{\psi}_{l\tau}\right\rangle \equiv& \left\{\tilde{V}_{\mathrm{H}}[\tilde{n}_{kl\tau}+\hat{n}_{kl\tau}]+\frac{\delta^2 E_{\mathrm{xc}}}{\delta n^\sigma \delta n^\tau}(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})\right\}\left|\tilde{\psi}_{j\sigma}\right\rangle + \sum_{IJ}|\tilde{p}_I\rangle\hat{D}_{IJ}\left[\tilde{V}_{\mathrm{H}}[\tilde{n}_{kl\tau}+\hat{n}_{kl\tau}]+\frac{\delta^2 E_{\mathrm{xc}}}{\delta n^\sigma \delta n^\tau}(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})\right]\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle \\ &+\sum_{IJ,I'J'}|\tilde{p}_I\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle\frac{\delta^2\left(E^1-\tilde{E}^1\right)}{\delta\rho_{IJ}^\sigma\delta\rho_{I'J'}^\tau}\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{l\tau}\right\rangle - \delta_{\sigma\tau}\left\{\tilde{V}_{\mathrm{EX}}\left[\tilde{n}_{kj\sigma}+\hat{n}_{kj\sigma}\right]\left|\tilde{\psi}_{l\sigma}\right\rangle + \sum_{IJ}|\tilde{p}_I\rangle\hat{D}_{IJ}\left[\tilde{V}_{\mathrm{EX}}\right]\left\langle\tilde{p}_J\middle|\tilde{\psi}_{l\sigma}\right\rangle\right. \\ &\left.+\sum_{(I,K)(J,L)}\left(K^1_{IJLK}-\tilde{K}^1_{IJLK}\right)|\tilde{p}_I\rangle\left\langle\tilde{p}_K\middle|\tilde{\psi}_{j\sigma}\right\rangle\left\langle\tilde{\psi}_{k\sigma}\middle|\tilde{p}_L\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{l\sigma}\right\rangle\right\} \end{aligned} \tag{20}$$

and the orbitals via the derivative of the kernel functional as

$$\begin{aligned}\left\langle\tilde{\psi}_{j\sigma}\middle|\tilde{K}'_{\sigma\tau\tau'}\middle|\tilde{\psi}_{k\tau}\tilde{\psi}_{l\tau}\tilde{\psi}_{k'\tau'}\tilde{\psi}_{l'\tau'}\right\rangle \equiv& \frac{\delta^3 E_{\mathrm{xc}}}{\delta n^\sigma \delta n^\tau \delta n^{\tau'}}(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})(\tilde{n}_{k'l'\tau'}+\hat{n}_{k'l'\tau'})\left|\tilde{\psi}_{j\sigma}\right\rangle \\ &+\sum_{IJ}|\tilde{p}_I\rangle\hat{D}_{IJ}\left[\frac{\delta^3 E_{\mathrm{xc}}}{\delta n^\sigma \delta n^\tau \delta n^{\tau'}}(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})(\tilde{n}_{k'l'\tau'}+\hat{n}_{k'l'\tau'})\right]\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle \\ &+\sum_{IJ,I'J',I''J''}|\tilde{p}_I\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle\frac{\delta^3\left(E^1-\tilde{E}^1\right)}{\delta\rho_{IJ}^\sigma\delta\rho_{I'J'}^\tau\delta\rho_{I''J''}^{\tau'}}\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{l\tau}\right\rangle\left\langle\tilde{\psi}_{k'\tau'}\middle|\tilde{p}_{I''}\right\rangle\left\langle\tilde{p}_{J''}\middle|\tilde{\psi}_{l'\tau'}\right\rangle, \end{aligned} \tag{21}$$

where $\tilde{V}_{\mathrm{H}}$ is the Hartree potential and E_{xc} is the local exchange-correlation functional.

Under the harmonic perturbing potential with a set of frequencies $\{\omega_{\bar{a}}\}$,

$$\delta\tilde{V}_{\mathrm{ext}}(t)=\sum_{\bar{a}}\left[\tilde{V}^+_{\bar{a}}e^{i\omega_{\bar{a}}t}+\tilde{V}^-_{\bar{a}}e^{-i\omega_{\bar{a}}t}\right], \tag{22}$$

the first- and second-order TDKS orbitals can be expressed as

$$\left|\tilde{\psi}^{(1)}_{i\sigma}\right\rangle=\sum_{\bar{a}}\left[\left|\tilde{\psi}^+_{i\sigma,\bar{a}}\right\rangle e^{i\omega_{\bar{a}}t}+\left|\tilde{\psi}^-_{i\sigma,\bar{a}}\right\rangle e^{-i\omega_{\bar{a}}t}\right] \tag{23}$$

and

$$\begin{aligned}\left|\tilde{\psi}^{(2)}_{i\sigma}\right\rangle=\sum_{\bar{a}\bar{b}}\Big[&\left|\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}}\right\rangle e^{i(\omega_{\bar{a}}+\omega_{\bar{b}})t}+\left|\tilde{\psi}^{+-}_{i\sigma,\bar{a}\bar{b}}\right\rangle e^{i(\omega_{\bar{a}}-\omega_{\bar{b}})t} \\ &+\left|\tilde{\psi}^{-+}_{i\sigma,\bar{a}\bar{b}}\right\rangle e^{i(-\omega_{\bar{a}}+\omega_{\bar{b}})t}+\left|\tilde{\psi}^{--}_{i\sigma,\bar{a}\bar{b}}\right\rangle e^{i(-\omega_{\bar{a}}-\omega_{\bar{b}})t}\Big]. \end{aligned} \tag{24}$$

Substituting Eq. (23) into Eq. (18) and collecting the coefficient of $e^{\pm i\omega_{\bar{a}}t}$, we can obtain the first-order TDKS equation for the frequency-dependent orbitals $\left|\tilde{\psi}^\pm_{i\sigma,\bar{a}}\right\rangle$,

$$\begin{aligned}\tilde{H}^\sigma\left|\tilde{\psi}^\pm_{i\sigma,\bar{a}}\right\rangle &+\sum_{j\tau}\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^\pm_{j\tau,\bar{a}}\right\rangle+\sum_{j\tau}\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^\mp_{j\tau,\bar{a}}\tilde{\psi}_{j\tau}\right\rangle \\ &+[\tilde{V}^\pm_{\bar{a}},\tilde{\gamma}^\sigma]\left|\tilde{\psi}_{i\sigma}\right\rangle=\epsilon_{i\sigma}\tilde{S}\left|\tilde{\psi}^\pm_{i\sigma,\bar{a}}\right\rangle\mp\omega_a\tilde{S}\left|\tilde{\psi}^\pm_{i\sigma,\bar{a}}\right\rangle, \end{aligned} \tag{25}$$

where $\tilde{\gamma}^\sigma=\sum_i\left|\tilde{\psi}_{i\sigma}\right\rangle\left\langle\tilde{\psi}_{i\sigma}\right|$ is the zero-order density matrix. Due to the orthonormality constrains of TDKS orbitals, we have $\left\langle\tilde{\psi}_{j\sigma}\middle|\tilde{S}\middle|\tilde{\psi}^+_{i\sigma,\bar{a}}\right\rangle+\left\langle\tilde{\psi}^-_{j\sigma,\bar{a}}\middle|\tilde{S}\middle|\tilde{\psi}_{i\sigma}\right\rangle=0$. According to the parallel transport gauge in TDDFT,[40] the first-order TDKS orbitals can be chosen to be orthogonal to the subspace spanned by the occupied orbitals, i.e., $\left\langle\tilde{\psi}_{j\sigma}\middle|\tilde{S}\middle|\tilde{\psi}^\pm_{i\sigma,\bar{a}}\right\rangle=0$. Thus, Eq. (25) is solved in the subspace spanned by the virtual KS orbitals. By introducing the projection operator $\tilde{P}^\sigma_c=1-\sum_i\tilde{S}\left|\tilde{\psi}_{i\sigma}\right\rangle\left\langle\tilde{\psi}_{i\sigma}\right|$, Eq. (25) can be cast into the form of a linear matrix equation,

$$\left[\begin{pmatrix}\tilde{\mathbf{A}}&\tilde{\mathbf{B}}\\ \tilde{\mathbf{B}}&\tilde{\mathbf{A}}\end{pmatrix}+\omega_{\bar{a}}\begin{pmatrix}\tilde{\mathbf{S}}&\mathbf{0}\\ \mathbf{0}&-\tilde{\mathbf{S}}\end{pmatrix}\right]\begin{pmatrix}\tilde{\mathbf{\Psi}}^+_{\bar{a}}\\ \tilde{\mathbf{\Psi}}^-_{\bar{a}}\end{pmatrix}=-\begin{pmatrix}\tilde{\mathbf{P}}_{\mathbf{c}}[\tilde{\mathbf{V}}^+_{\bar{a}},\tilde{\boldsymbol{\gamma}}]\tilde{\mathbf{\Psi}}\\ \tilde{\mathbf{P}}_{\mathbf{c}}[\tilde{\mathbf{V}}^-_{\bar{a}},\tilde{\boldsymbol{\gamma}}]\tilde{\mathbf{\Psi}}\end{pmatrix}, \tag{26}$$

where the operators $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{B}}$ act on the orbitals according to the following equations:

$$\begin{aligned}\left[\tilde{\mathbf{A}}\tilde{\mathbf{\Psi}}^\pm\right]_{i\sigma}&=\sum_j\left(\tilde{H}^\sigma\delta_{ij}-\epsilon_{ij\sigma}\tilde{S}\right)\left|\tilde{\psi}^\pm_{j\sigma}\right\rangle \\ &\quad+\sum_{j\tau}\left\langle\tilde{P}^\sigma_c\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{P}^\tau_c\tilde{\psi}^\pm_{j\tau}\right\rangle, \\ \left[\tilde{\mathbf{B}}\tilde{\mathbf{\Psi}}^\pm\right]_{i\sigma}&=\sum_{j\tau}\left\langle\tilde{P}^\sigma_c\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{P}^\tau_c\tilde{\psi}^\pm_{j\tau}\tilde{\psi}_{j\tau}\right\rangle. \end{aligned} \tag{27}$$

The energy ω_α and first-order TDKS orbitals $\left|\tilde{\psi}^\pm_{i\sigma,\alpha}\right\rangle$ of the αth excited state can be determined as the poles of the linear response function where Eq. (26) becomes singular. Based on the spectral properties[41] of the response operators $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{B}}$, the inverse of the super-matrix in Eq. (26) is equal to

$$\begin{aligned}\left[\begin{pmatrix}\tilde{\mathbf{A}}&\tilde{\mathbf{B}}\\ \tilde{\mathbf{B}}&\tilde{\mathbf{A}}\end{pmatrix}+\omega_{\bar{a}}\begin{pmatrix}\tilde{\mathbf{S}}&\mathbf{0}\\ \mathbf{0}&-\tilde{\mathbf{S}}\end{pmatrix}\right]^{-1}=\sum_\alpha\Bigg\{&\frac{1}{\omega_\alpha-\omega_{\bar{a}}}\begin{pmatrix}\tilde{\mathbf{\Psi}}^+_\alpha\\ \tilde{\mathbf{\Psi}}^-_\alpha\end{pmatrix}\begin{pmatrix}\tilde{\mathbf{\Psi}}^+_\alpha&\tilde{\mathbf{\Psi}}^-_\alpha\end{pmatrix} \\ &+\frac{1}{\omega_\alpha+\omega_{\bar{a}}}\begin{pmatrix}\tilde{\mathbf{\Psi}}^-_\alpha\\ \tilde{\mathbf{\Psi}}^+_\alpha\end{pmatrix}\begin{pmatrix}\tilde{\mathbf{\Psi}}^-_\alpha&\tilde{\mathbf{\Psi}}^+_\alpha\end{pmatrix}\Bigg\}. \end{aligned} \tag{28}$$

Substituting Eq. (28) into Eq. (26), one can express the first-order TDKS orbitals at frequency ω_a as a linear combination of the excited states,

$$\begin{pmatrix}\tilde{\mathbf{\Psi}}^+_{\bar{a}}\\ \tilde{\mathbf{\Psi}}^-_{\bar{a}}\end{pmatrix}=-\sum_\alpha\left\{\frac{V^{\bar{a}}_{0\alpha}}{\omega_\alpha-\omega_{\bar{a}}}\begin{pmatrix}\tilde{\mathbf{\Psi}}^+_\alpha\\ \tilde{\mathbf{\Psi}}^-_\alpha\end{pmatrix}+\frac{V^{\bar{a}}_{\alpha 0}}{\omega_\alpha+\omega_{\bar{a}}}\begin{pmatrix}\tilde{\mathbf{\Psi}}^-_\alpha\\ \tilde{\mathbf{\Psi}}^+_\alpha\end{pmatrix}\right\}, \tag{29}$$

where $V^{\bar{a}}_{0\alpha}=\sum_{i\sigma}\left[\left\langle\tilde{\psi}^+_{i\sigma,\alpha}\middle|\tilde{V}^+_{\bar{a}}\middle|\tilde{\psi}_{i\sigma}\right\rangle+\left\langle\tilde{\psi}^-_{i\sigma,\alpha}\middle|\tilde{V}^-_{\bar{a}}\middle|\tilde{\psi}_{i\sigma}\right\rangle\right]$ and equals to $\langle\Psi_0|\hat{V}^+_{\bar{a}}|\Psi_\alpha\rangle$ obtained in Sec. II A.

By substituting Eq. (24) into Eq. (19) and collecting the coefficient of $e^{\pm i(\omega_{\bar{a}}+\omega_{\bar{b}})t}$, one arrives at the second-order TDKS equation for the frequency-dependent orbitals $\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle$,

$$\tilde{H}^{\sigma}\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle + \sum_{j\tau}\left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm\pm}_{j\tau,\bar{a}\bar{b}}\right\rangle + \sum_{j\tau}\left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp\mp}_{j\tau,\bar{a}\bar{b}}\tilde{\psi}_{j\tau}\right\rangle + \left\{\sum_{j\tau}\left\langle\tilde{\psi}^{\pm}_{i\sigma,\bar{a}}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{b}}\right\rangle + \sum_{j\tau}\left\langle\tilde{\psi}^{\pm}_{i\sigma,\bar{a}}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{b}}\tilde{\psi}_{j\tau}\right\rangle + \sum_{j\tau}\left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}^{\pm}_{j\tau,\bar{b}}\right\rangle + \left(\bar{a}\leftrightarrow\bar{b}\right)\right\} + \sum_{jj'\tau\tau'}\left[\left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}_{j\tau}\tilde{\psi}^{\mp}_{j'\tau',\bar{b}}\tilde{\psi}_{j'\tau'}\right\rangle + \left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}_{j\tau}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\pm}_{j'\tau',\bar{b}}\right\rangle + \left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{a}}\tilde{\psi}^{\mp}_{j'\tau',\bar{b}}\tilde{\psi}_{j'\tau'}\right\rangle + \left\langle\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{a}}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\pm}_{j'\tau',\bar{b}}\right\rangle\right] + \left\{\tilde{V}^{\pm}_{\bar{a}}\left|\tilde{\psi}^{\pm}_{i\sigma,\bar{b}}\right\rangle + \left(\bar{a}\leftrightarrow\bar{b}\right)\right\} = \epsilon_{i\sigma}\tilde{S}\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle \mp (\omega_{\bar{a}}+\omega_{\bar{b}})\tilde{S}\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle. \tag{30}$$

Here, $\left(\bar{a}\leftrightarrow\bar{b}\right)$ indicates the same expression but with the indices $\bar{a}$ and $\bar{b}$ interchanged. Based on the orthonormality constrains of the TDKS orbitals, the projection of $\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle$ into the subspace of the occupied KS orbitals is given by

$$\left\langle\tilde{\psi}_{j\sigma}\left|\tilde{S}\right|\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}}\right\rangle + \left\langle\tilde{\psi}^{--}_{j\sigma,\bar{a}\bar{b}}\left|\tilde{S}\right|\tilde{\psi}_{i\sigma}\right\rangle = -\left\langle\tilde{\psi}^{-}_{j\sigma,\bar{a}}\left|\tilde{S}\right|\tilde{\psi}^{+}_{i\sigma,\bar{b}}\right\rangle - \left\langle\tilde{\psi}^{-}_{j\sigma,\bar{b}}\left|\tilde{S}\right|\tilde{\psi}^{+}_{i\sigma,\bar{a}}\right\rangle. \tag{31}$$

The projection of $\left|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle$ into the subspace of the virtual KS orbitals can be obtained by applying $\tilde{P}^{\sigma}_{c}$ onto both sides of Eq. (30), which leads to a linear matrix equation as

$$\left[\begin{pmatrix}\tilde{\mathbf{A}} & \tilde{\mathbf{B}}\\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}}\end{pmatrix} + (\omega_{\bar{a}}+\omega_{\bar{b}})\begin{pmatrix}\tilde{\mathbf{S}} & \mathbf{0}\\ \mathbf{0} & -\tilde{\mathbf{S}}\end{pmatrix}\right]\begin{pmatrix}\tilde{\mathbf{P}}_{\mathbf{c}}\tilde{\boldsymbol{\Psi}}^{++}_{\bar{a}\bar{b}}\\ \tilde{\mathbf{P}}_{\mathbf{c}}\tilde{\boldsymbol{\Psi}}^{--}_{\bar{a}\bar{b}}\end{pmatrix} = \begin{pmatrix}\tilde{\mathbf{S}}\tilde{\mathbf{V}}^{+}_{\bar{a}\bar{b}}\\ \tilde{\mathbf{S}}\tilde{\mathbf{V}}^{-}_{\bar{a}\bar{b}}\end{pmatrix}, \tag{32}$$

where

$$\begin{aligned}\tilde{S}\left|\tilde{V}^{\pm}_{i\sigma,\bar{a}\bar{b}}\right\rangle = {}& \sum_{jk\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{j\tau}\tilde{\psi}_{k\tau}\right\rangle\left\{\left\langle\tilde{\psi}^{\mp}_{k\tau,\bar{a}}\left|\tilde{S}\right|\tilde{\psi}^{\pm}_{j\tau,\bar{b}}\right\rangle - \left\langle\tilde{\psi}^{\mp}_{k\tau,\bar{b}}\left|\tilde{S}\right|\tilde{\psi}^{\pm}_{j\tau,\bar{a}}\right\rangle\right\} - \left\{\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\pm}_{i\sigma,\bar{a}}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{b}}\right\rangle\right.\\ & + \sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\pm}_{i\sigma,\bar{a}}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{b}}\tilde{\psi}_{j\tau}\right\rangle + \sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}^{\pm}_{j\tau,\bar{b}}\right\rangle + \left(\bar{a}\leftrightarrow\bar{b}\right)\Bigg\}\\ & + \left\{\sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\pm}_{j\sigma,\bar{a}}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{k\tau}\tilde{\psi}^{\pm}_{k\tau,\bar{b}}\right\rangle + \sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\pm}_{j\sigma,\bar{a}}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}^{\mp}_{k\tau,\bar{b}}\tilde{\psi}_{k\tau}\right\rangle + \left(\bar{a}\leftrightarrow\bar{b}\right)\right\}\\ & + \sum_{jj'\tau\tau'}\left[\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}_{j\tau}\tilde{\psi}^{\mp}_{j'\tau',\bar{b}}\tilde{\psi}_{j'\tau'}\right\rangle + \left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}^{\mp}_{j\tau,\bar{a}}\tilde{\psi}_{j\tau}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\pm}_{j'\tau',\bar{b}}\right\rangle + \left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{a}}\tilde{\psi}^{\mp}_{j'\tau',\bar{b}}\tilde{\psi}_{j'\tau'}\right\rangle\right.\\ & \left.\left.+\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\left|\tilde{K}'_{\sigma\tau\tau'}\right|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\bar{a}}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\pm}_{j'\tau',\bar{b}}\right\rangle\right] - \left\{\tilde{P}^{\sigma}_{c}[\tilde{V}^{\pm}_{\bar{a}},\tilde{\gamma}^{\sigma\pm}_{\bar{b}}]\left|\tilde{\psi}_{i\sigma}\right\rangle + \left(\bar{a}\leftrightarrow\bar{b}\right)\right\}.\end{aligned} \tag{33}$$

Here, $\tilde{\gamma}^{\sigma\pm}_{\bar{a}} = \sum_i\left(\left|\tilde{\psi}_{i\sigma}\right\rangle\left\langle\tilde{\psi}^{\mp}_{i\sigma,\bar{a}}\right| + \left|\tilde{\psi}^{\pm}_{i\sigma,\bar{a}}\right\rangle\left\langle\tilde{\psi}_{i\sigma}\right|\right)$ is the first-order density matrix at frequency $\pm\omega_{\bar{a}}$.

D. Nonadiabatic coupling in TDDFT

We are now ready to derive the residues of the auxiliary couplings within TDDFT and to obtain explicit expressions of NAC with the TDKS orbitals. In TDDFT, the auxiliary couplings are defined as

$$\tilde{C}(t) = \sum_{i\sigma}\left\langle\tilde{\psi}_{i\sigma}(t)\left|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\right|\tilde{\psi}_{i\sigma}(t)\right\rangle. \tag{34}$$

Substituting Eq. (17) into Eq. (34) and collecting the coefficients of $e^{i\omega_{\bar{a}}t}$, one obtains the first-order auxiliary coupling at frequency $\omega_{\bar{a}}$ as

$$\tilde{C}^{(1)}(\omega_{\bar{a}}) = \sum_{i\sigma}\left\langle\tilde{\psi}_{i\sigma}\left|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\right|\tilde{\psi}^{+}_{i\sigma,\bar{a}}\right\rangle + \sum_{i\sigma}\left\langle\tilde{\psi}^{-}_{i\sigma,\bar{a}}\left|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\right|\tilde{\psi}_{i\sigma}\right\rangle. \tag{35}$$

Using Eq. (29), the residue of $\tilde{C}^{(1)}(\omega_{\bar{a}})$ at frequency ω_{α} can be expressed as

$$\lim_{\omega_{\bar{a}}\to\omega_{\alpha}}(\omega_{\alpha}-\omega_{\bar{a}})\tilde{C}^{(1)}(\omega_{\bar{a}}) = V^{\bar{a}}_{0\alpha}\sum_{i\sigma}\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha} - \tilde{\psi}^{-}_{i\sigma,\alpha}\left|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\right|\tilde{\psi}_{i\sigma}\right\rangle. \tag{36}$$

Comparing Eq. (9) and Eq. (36), one can immediately arrive at NAC between the ground state and the αth excited state,

$$g^{x}_{0\alpha} = \sum_{i\sigma}\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha} - \tilde{\psi}^{-}_{i\sigma,\alpha}\left|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\right|\tilde{\psi}_{i\sigma}\right\rangle. \tag{37}$$

Next, we derive NAC between the excited states based on the second-order auxiliary coupling. Substituting Eq. (17) into Eq. (34) and collecting the coefficients of $e^{i(\omega_{\bar{a}}+\omega_{\bar{b}})t}$, one obtains the second-order auxiliary coupling at frequencies $\omega_{\bar{a}}$ and $\omega_{\bar{b}}$,

$$\tilde{C}^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}}) = \sum_{i\sigma}\frac{d}{dx}\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{S}\middle|\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}}\right\rangle + \sum_{i\sigma}\left\langle\tilde{\psi}^{-}_{i\sigma,\bar{a}}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}^{+}_{i\sigma,\bar{b}}\right\rangle + \sum_{i\sigma}\left\langle\tilde{\psi}^{-}_{i\sigma,\bar{b}}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}^{+}_{i\sigma,\bar{a}}\right\rangle - \sum_{i\sigma}\left\langle\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}} - \tilde{\psi}^{--}_{i\sigma,\bar{a}\bar{b}}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle. \tag{38}$$

Following Eqs. (29) and (31), the residue of the first three terms (denoted by $\{1\sim3\}$) on the right-hand side of Eq. (38) at frequencies $\omega_{\bar{a}} = \omega_\alpha$ and $\omega_{\bar{b}} = -\omega_\beta$ can be calculated by

$$\begin{aligned}\lim_{\omega_{\bar{a}}\to\omega_\alpha,\omega_{\bar{b}}\to-\omega_\beta}(\omega_\alpha-\omega_{\bar{a}})\left(\omega_\beta+\omega_{\bar{b}}\right)C^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}})\{1\sim3\} &= -V^{\bar{a}}_{0\alpha}V^{\bar{b}}_{\beta0}\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right]\\ &= -V^{\bar{a}}_{0\alpha}V^{\bar{b}}_{\beta0}\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\left(\frac{\mathcal{T}^{\dagger}d\mathcal{T}}{dx}\right)\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\left(\frac{\mathcal{T}^{\dagger}d\mathcal{T}}{dx}\right)\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right]\\ &\quad - V^{\bar{a}}_{0\alpha}V^{\bar{b}}_{\beta0}\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\frac{d}{dx}\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\frac{d}{dx}\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right].\end{aligned} \tag{39}$$

Here, $\left(\mathcal{T}^{\dagger}d\mathcal{T}/dx\right)$ indicates the explicit derivative of operator $\mathcal{T}$ with respect to x, and the derivatives of the first-order TDKS orbitals are not involved. To arrive at Eq. (39), we have employed the orthogonality condition,

$$\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right] = -\delta_{\alpha\beta}. \tag{40}$$

Given that $\left|\tilde{\psi}^{\pm}_{i\sigma,\alpha}\right\rangle$ is the eigenstate of the super-matrix in Eq. (26), one can easily prove the following equation:

$$\begin{aligned}\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\frac{d}{dx}\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\frac{d}{dx}\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right] &= \omega^{-1}_{\beta\alpha}\begin{pmatrix}\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\alpha}} & \tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\alpha}}\end{pmatrix}\left[\begin{pmatrix}\tilde{\mathbf{A}} & \tilde{\mathbf{B}}\\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}}\end{pmatrix} + \omega_\beta\begin{pmatrix}\tilde{\mathbf{S}} & \mathbf{0}\\ \mathbf{0} & -\tilde{\mathbf{S}}\end{pmatrix}\right]\begin{pmatrix}d\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\beta}}/dx\\ d\tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\beta}}/dx\end{pmatrix}\\ &= -\omega^{-1}_{\beta\alpha}\begin{pmatrix}\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\alpha}} & \tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\alpha}}\end{pmatrix}\left\{\frac{d}{dx}\left[\begin{pmatrix}\tilde{\mathbf{A}} & \tilde{\mathbf{B}}\\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}}\end{pmatrix} + \omega_\beta\begin{pmatrix}\tilde{\mathbf{S}} & \mathbf{0}\\ \mathbf{0} & -\tilde{\mathbf{S}}\end{pmatrix}\right]\right\}\begin{pmatrix}\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\beta}}\\ \tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\beta}}\end{pmatrix} = -\omega^{-1}_{\beta\alpha}\left.\frac{d\mathcal{M}_{\alpha\beta}}{dx}\right|_{\tilde{\psi}^{\pm}_{\alpha},\tilde{\psi}^{\pm}_{\beta}},\end{aligned} \tag{41}$$

where we have introduced the following variables:

$$\begin{aligned}\omega_{\beta\alpha} &\equiv \omega_\beta - \omega_\alpha,\\ \mathcal{M}_{\alpha\beta} &\equiv \begin{pmatrix}\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\alpha}} & \tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\alpha}}\end{pmatrix}\left[\begin{pmatrix}\tilde{\mathbf{A}} & \tilde{\mathbf{B}}\\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}}\end{pmatrix} + \omega_\beta\begin{pmatrix}\tilde{\mathbf{S}} & \mathbf{0}\\ \mathbf{0} & -\tilde{\mathbf{S}}\end{pmatrix}\right]\begin{pmatrix}\tilde{\boldsymbol{\psi}}^{+}_{\boldsymbol{\beta}}\\ \tilde{\boldsymbol{\psi}}^{-}_{\boldsymbol{\beta}}\end{pmatrix}.\end{aligned} \tag{42}$$

Considering that the second-order TDKS orbital $|\tilde{\psi}^{\pm\pm}_{i\sigma,\bar{a}\bar{b}}\rangle$ can be split into two parts: one is the projection onto the subspace of the occupied KS orbitals and the other one is the projection onto the subspace of the virtual KS orbitals. The fourth term (denoted by $\{4\}$) on the right-hand side of Eq. (38) can be expressed as

$$\tilde{C}^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}})\{4\} = -\sum_{i\sigma}\left\langle\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}} - \tilde{\psi}^{--}_{i\sigma,\bar{a}\bar{b}}\middle|\tilde{P}^{\sigma}_{c}\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle - \sum_{ij\sigma}\left\langle\tilde{\psi}^{++}_{i\sigma,\bar{a}\bar{b}} - \tilde{\psi}^{--}_{i\sigma,\bar{a}\bar{b}}\middle|\tilde{S}\middle|\tilde{\psi}_{j\sigma}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle. \tag{43}$$

Using Eqs. (29), (31), and (32), the residue of $\tilde{C}^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}})\{4\}$ at frequencies $\omega_{\bar{a}} = \omega_\alpha$ and $\omega_{\bar{b}} = -\omega_\beta$ is given by

$$\begin{aligned}\lim_{\omega_{\bar{a}}\to\omega_\alpha,\omega_{\bar{b}}\to-\omega_\beta}(\omega_\alpha-\omega_{\bar{a}})\left(\omega_\beta+\omega_{\bar{b}}\right)\tilde{C}^{(2)}(\omega_{\bar{a}},\omega_{\bar{b}})\{4\} &= V^{\bar{a}}_{0\alpha}V^{\bar{b}}_{\beta0}\sum_{ij\sigma}\left[\left\langle\tilde{\psi}^{+}_{j\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle + \left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right]\left\langle\tilde{\psi}_{i\sigma}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{j\sigma}\right\rangle\\ &\quad - V^{\bar{a}}_{0\alpha}V^{\bar{b}}_{\beta0}\sum_{i\sigma}\left\langle\tilde{T}^{+}_{i\sigma,\alpha\beta} - \tilde{T}^{-}_{i\sigma,\alpha\beta}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle.\end{aligned} \tag{44}$$

Here, $\tilde{T}^{\pm}_{i\sigma,\alpha\beta}$ can be determined by the following linear matrix equation:

$$\left[\begin{pmatrix}\tilde{\mathbf{A}} & \tilde{\mathbf{B}}\\ \tilde{\mathbf{B}} & \tilde{\mathbf{A}}\end{pmatrix} + \left(\omega_\alpha-\omega_\beta\right)\begin{pmatrix}\tilde{\mathbf{S}} & \mathbf{0}\\ \mathbf{0} & -\tilde{\mathbf{S}}\end{pmatrix}\right]\begin{pmatrix}\tilde{\mathbf{T}}^{+}_{\boldsymbol{\alpha\beta}}\\ \tilde{\mathbf{T}}^{-}_{\boldsymbol{\alpha\beta}}\end{pmatrix} = \begin{pmatrix}\tilde{\mathbf{S}}\tilde{\mathbf{V}}^{+}_{\boldsymbol{\alpha\beta}}\\ \tilde{\mathbf{S}}\tilde{\mathbf{V}}^{-}_{\boldsymbol{\alpha\beta}}\end{pmatrix}, \tag{45}$$

where the expression of $\tilde{\mathbf{S}}\tilde{\mathbf{V}}^{+}_{\alpha\beta}$ and $\tilde{\mathbf{S}}\tilde{\mathbf{V}}^{-}_{\alpha\beta}$ is shown in Eq. (A2) of the Appendix. Finally, combining Eqs. (10), (39), (41), and (44), one can express the NAC between the αth and the βth excited states as

$$g^{x}_{\alpha\beta} = \omega^{-1}_{\beta\alpha}\frac{d\mathcal{M}_{\alpha\beta}}{dx}\bigg|_{\tilde{\psi}^{\pm}_{\alpha},\tilde{\psi}^{\pm}_{\beta}} - \sum_{i\sigma}\left\langle \tilde{T}^{+}_{i\sigma,\alpha\beta} - \tilde{T}^{-}_{i\sigma,\alpha\beta}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle - \sum_{i\sigma}\left[\left\langle \tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\left(\frac{\mathcal{T}^{\dagger}d\mathcal{T}}{dx}\right)\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\left(\frac{\mathcal{T}^{\dagger}d\mathcal{T}}{dx}\right)\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right]$$
$$+ \sum_{ij\sigma}\left[\left\langle \tilde{\psi}^{+}_{j\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle + \left\langle \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right]\left\langle \tilde{\psi}_{i\sigma}\middle|\mathcal{T}^{\dagger}\frac{d}{dx}\mathcal{T}\middle|\tilde{\psi}_{j\sigma}\right\rangle. \tag{46}$$

In Eqs. (37) and (46), the evaluation of $g^{x}_{0\alpha}$ and $g^{x}_{\alpha\beta}$ involves the derivatives of the KS orbitals with respect to every ionic coordinate x. In principle, these derivatives can be computed by solving the self-consistent Sternheimer equation[42] based on the density functional perturbation theory.[43,44] However, for a large system composed of many ions (or x) and KS orbitals, the derivative calculations can be prohibitively expensive. Instead, we will resort to the following Lagrangian formulation[45,46] to compute the NAC matrix elements. The Lagrangian formulation can avoid the derivative calculations of the KS orbitals with respect to x entirely, thus drastically reducing the computational cost.[47,48]

E. Lagrangian formulation

1. NAC $g^{x}_{0\alpha}$

The Lagrangian for the NAC matrix elements between the ground and excited states can be constructed as

$$\hat{\mathcal{L}}_{0\alpha}\left[x,\tilde{\psi},\tilde{\mathbf{Z}},\mathbf{\Gamma}\right] = \sum_{i\sigma}\left\langle \tilde{\psi}^{+}_{i\sigma,\alpha} - \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}_{i\sigma}\right\rangle + \sum_{ij\sigma}\left\langle \tilde{Z}_{i\sigma}\middle|\left(\tilde{H}^{\sigma}\delta_{ij} - \epsilon_{ij\sigma}\tilde{S}\right)\middle|\tilde{\psi}_{j\sigma}\right\rangle - \sum_{i\geq j,\sigma}\Gamma_{ij\sigma}\left(\left\langle \tilde{\psi}_{i\sigma}\middle|\tilde{S}\middle|\tilde{\psi}_{j\sigma}\right\rangle - \delta_{ij}\right), \tag{47}$$

by enforcing both the Brillouin condition, Eq. (15), and the orthonormal condition for the KS orbitals. $\tilde{\mathbf{Z}}$ is the well-known Z-vector.[49] The multipliers $\tilde{\mathbf{Z}}$ and $\mathbf{\Gamma}$ are determined from the stationary condition of the Lagrangian functional, i.e., $\delta\hat{\mathcal{L}}_{0\alpha}/\delta\tilde{\psi}_{i\sigma} = 0$, and they can be solved by projections onto both the space spanned by the virtual KS orbitals and the space spanned by the occupied KS orbitals. The first projection leads to a linear equation,

$$\left[\left(\tilde{\mathbf{A}} + \tilde{\mathbf{B}}\right)\tilde{\mathbf{Z}}\right]_{i\sigma} = -\tilde{S}\left|\tilde{\psi}^{+}_{i\sigma,\alpha} - \tilde{\psi}^{-}_{i\sigma,\alpha}\right\rangle, \tag{48}$$

and we immediately have

$$\left|\tilde{Z}_{i\sigma}\right\rangle = \omega^{-1}_{\alpha}\left|\tilde{\psi}^{+}_{i\sigma,\alpha} + \tilde{\psi}^{-}_{i\sigma,\alpha}\right\rangle. \tag{49}$$

The second projection yields the solution of $\Gamma_{ij\sigma}$ according to

$$\left(1+\delta_{ij}\right)\Gamma_{ij\sigma} = \omega^{-1}_{\alpha}\sum_{k\tau}\left[\left\langle \tilde{\psi}_{i\sigma}\tilde{\psi}_{j\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{k\tau}\left(\tilde{\psi}^{+}_{k\tau,\alpha} + \tilde{\psi}^{-}_{k\tau,\alpha}\right)\right\rangle + \left\langle \tilde{\psi}_{i\sigma}\tilde{\psi}_{j\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\left(\tilde{\psi}^{+}_{k\tau,\alpha} + \tilde{\psi}^{-}_{k\tau,\alpha}\right)\tilde{\psi}_{k\tau}\right\rangle\right]. \tag{50}$$

Once $\tilde{\mathbf{Z}}$ and $\mathbf{\Gamma}$ are obtained, the NAC matrix elements are simply the *partial* derivatives of the Lagrangian functional with respect to x,

$$g^{x}_{0\alpha} = \frac{\partial\hat{\mathcal{L}}_{0\alpha}}{\partial x} = \sum_{i\sigma}\left\langle \tilde{\psi}^{+}_{i\sigma,\alpha} - \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle + \omega^{-1}_{\alpha}\sum_{ij\sigma}\left\langle \tilde{\psi}^{+}_{i\sigma,\alpha} + \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\frac{\partial\left(\tilde{H}^{\sigma}\delta_{ij} - \epsilon_{ij\sigma}\tilde{S}\right)}{\partial x}\middle|\tilde{\psi}_{j}\right\rangle - \sum_{i\geq j,\sigma}\Gamma_{ij\sigma}\left\langle \tilde{\psi}_{i\sigma}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}_{j\sigma}\right\rangle. \tag{51}$$

Here $\partial/\partial x$ indicates the partial derivative with respect to x; the derivatives of KS orbitals with respect to x, $\left|d\tilde{\psi}_{i\sigma}/dx\right\rangle$, are no longer involved. Thus, the Lagrangian formulation enables much more expedient calculations of the NAC matrix elements. Note that one has to consider the explicit dependence of the PAW projector functions $\mathcal{T}$ on x when computing the partial derivatives. The expression of terms on the right-hand side of Eq. (51) can be found in Eqs. (A3) and (A4) of the Appendix.

2. NAC $g^{x}_{\alpha\beta}$

Similarly, the Lagrangian for the NAC matrix elements between two excited states can be written as

$$\hat{\mathcal{L}}_{\alpha\beta}\left[x,\tilde{\psi},\tilde{\mathbf{Z}},\mathbf{\Gamma}\right] = \omega^{-1}_{\beta\alpha}\mathcal{M}_{\alpha\beta} - \sum_{i\sigma}\left\langle \tilde{T}^{+}_{i\sigma,\alpha\beta} - \tilde{T}^{-}_{i\sigma,\alpha\beta}\middle|\tilde{S}\middle|\tilde{\psi}_{i\sigma}\right\rangle - \sum_{i\sigma}\left[\left\langle \tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle - \left\langle \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right] + \sum_{ij\sigma}\left[\left\langle \tilde{\psi}^{+}_{j\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle + \left\langle \tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right]\left\langle \tilde{\psi}_{i\sigma}\middle|\tilde{S}\middle|\tilde{\psi}_{j\sigma}\right\rangle + \sum_{ij\sigma}\left\langle \tilde{Z}_{i\sigma}\middle|\left(\tilde{H}^{\sigma}\delta_{ij} - \epsilon_{ij\sigma}\tilde{S}\right)\middle|\tilde{\psi}_{j\sigma}\right\rangle - \sum_{i\geq j,\sigma}\Gamma_{ij\sigma}\left(\left\langle \tilde{\psi}_{i\sigma}\middle|\tilde{S}\middle|\tilde{\psi}_{j\sigma}\right\rangle - \delta_{ij}\right). \tag{52}$$

The solution of $\delta\hat{\mathcal{L}}_{\alpha\beta}/\delta\tilde{\psi}_{i\sigma} = 0$ by projection onto the space spanned by the virtual KS orbitals leads to the following linear equation:

$$\left[\left(\tilde{\mathbf{A}} + \tilde{\mathbf{B}}\right)\tilde{\mathbf{Z}}\right]_{i\sigma} = \tilde{S}\left|\tilde{T}^{+}_{i\sigma,\alpha\beta} - \tilde{T}^{-}_{i\sigma,\alpha\beta}\right\rangle - \omega^{-1}_{\beta\alpha}\tilde{P}^{\sigma}_{c}\left|\frac{\delta\mathcal{M}_{\alpha\beta}}{\delta\tilde{\psi}_{i\sigma}}\right\rangle. \tag{53}$$

According to Eq. (45) and the fact that

$$\tilde{S}\left|\tilde{V}^{+}_{i\sigma,\alpha\beta}+\tilde{V}^{-}_{i\sigma,\alpha\beta}\right\rangle=-\tilde{P}^{\sigma}_{c}\left|\frac{\delta\mathcal{M}_{\alpha\beta}}{\delta\tilde{\psi}_{i\sigma}}\right\rangle, \tag{54}$$

we arrive immediately at

$$\left|\tilde{Z}_{i\sigma}\right\rangle=\omega^{-1}_{\beta\alpha}\left|\tilde{T}^{+}_{i\sigma,\alpha\beta}+\tilde{T}^{-}_{i\sigma,\alpha\beta}\right\rangle. \tag{55}$$

The projection onto the space spanned by the occupied KS orbitals yields the solution of $\Gamma_{ij\sigma}$ given by

$$\begin{aligned}\left(1+\delta_{ij}\right)\Gamma_{ij\sigma}=\omega^{-1}_{\beta\alpha}\left\langle\tilde{\psi}_{j\sigma}\left|\frac{\delta\mathcal{M}_{\alpha\beta}}{\delta\tilde{\psi}_{i\sigma}}\right.\right\rangle+\left[\left\langle\tilde{\psi}^{+}_{j\sigma,\alpha}\left|\tilde{S}\right|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\left|\tilde{S}\right|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right]+\omega^{-1}_{\beta\alpha}\sum_{k\tau}\left[\left\langle\tilde{\psi}_{i\sigma}\tilde{\psi}_{j\sigma}\left|\tilde{K}_{\sigma\tau}\right|\tilde{\psi}_{k\tau}\left(\tilde{T}^{+}_{i\sigma,\alpha\beta}+\tilde{T}^{-}_{i\sigma,\alpha\beta}\right)\right\rangle\right.\\ \left.+\left\langle\tilde{\psi}_{i\sigma}\tilde{\psi}_{j\sigma}\left|\tilde{K}_{\sigma\tau}\right|\left(\tilde{T}^{+}_{i\sigma,\alpha\beta}+\tilde{T}^{-}_{i\sigma,\alpha\beta}\right)\tilde{\psi}_{k\tau}\right\rangle\right].\end{aligned} \tag{56}$$

Finally, the NAC matrix elements between the excited states are evaluated as

$$\begin{aligned}g^{x}_{\alpha\beta}=\frac{\partial\hat{\mathcal{L}}_{\alpha\beta}}{\partial x}=\omega^{-1}_{\beta\alpha}\frac{\partial\mathcal{M}_{\alpha\beta}}{\partial x}-\sum_{i\sigma}\left\langle\tilde{T}^{+}_{i\sigma,\alpha\beta}-\tilde{T}^{-}_{i\sigma,\alpha\beta}\left|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\right|\tilde{\psi}_{i\sigma}\right\rangle-\sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\left|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\right|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle-\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\left|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\right|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right]\\ +\sum_{ij\sigma}\left[\left\langle\tilde{\psi}^{+}_{j\sigma,\alpha}\left|\tilde{S}\right|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\left|\tilde{S}\right|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right]\left\langle\tilde{\psi}_{i\sigma}\left|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\right|\tilde{\psi}_{j\sigma}\right\rangle+\omega^{-1}_{\beta\alpha}\sum_{i\sigma}\left\langle\tilde{T}^{+}_{i\sigma,\alpha\beta}+\tilde{T}^{-}_{i\sigma,\alpha\beta}\left|\frac{\partial\left(\tilde{H}^{\sigma}\delta_{ij}-\epsilon_{ij\sigma}\tilde{S}\right)}{\partial x}\right|\tilde{\psi}_{i\sigma}\right\rangle\\ -\sum_{i\geq j,\sigma}\Gamma_{ij\sigma}\left\langle\tilde{\psi}_{i\sigma}\left|\frac{\partial\tilde{S}}{\partial x}\right|\tilde{\psi}_{j\sigma}\right\rangle,\end{aligned} \tag{57}$$

where the partial derivative of $\mathcal{M}_{\alpha\beta}$ with respect to the ionic coordinate x can be found in Eq. (A5) of the Appendix.

III. NUMERICAL VALIDATIONS

The formulation presented here is general and can be implemented in any plane-wave PAW software package as a plug-and-compute module. In this work, the ground state calculations are carried out with the Vienna *Ab Initio* Simulation Package (VASP).[50,51] The ground state charge density and KS states are then taken as the input in our TDDFT formulation to compute the excited states and NAC matrix elements. To validate the present formulation, we calculate the NAC for two small molecules, LiH and HeH^+, which have been studied previously by the AO based NAC-TDDFT.[28] The spin-restricted ground state calculations are performed with supercell dimensions of 20 Å × 20 Å × 20 Å. The energy cutoff of the planewave basis is 400 eV for LiH and 600 eV for HeH^+. Here, the local adiabatic exchange-correlation functional with the Perdew–Burke–Ernzerhof generalized gradient approximation[52] is used and only Γ-point in the Brillouin zone is considered.

First, we calculate NAC g^{x}_{01} between the ground state $1^1\sum^+$ and the first excited state $2^1\sum^+$ in LiH with respect to the z coordinate of the H atom. The potential energy curves and NAC g^{x}_{01} as a function of the interatomic distance are shown in Fig. 1. We find that g^{x}_{01} first reaches a local maximum at a bond length of 1.1 Å, then a local minimum about the equilibrium bond length, and finally the maximum around 3.0 Å. Our results of g^{x}_{01} are very similar to those obtained by using the AO (cc-pVDZ) based NAC-TDDFT.[28]

Next, we examine the NAC between two well-separated excited states. The simple two-electron system HeH^+ is studied, and we compute the NAC g^{x}_{12} between the two lowest excited states with $^1\sum^+$ symmetry as a function of the bond length. The excitation energies of the two excited states as well as their difference are depicted in Fig. 2(a). The two states are well-separated with the bond length ranging from 0.6 Å to 2.5 Å. However, the energy gap between them coincides with the excitation energy of the first excited state at 1.5 Å, which

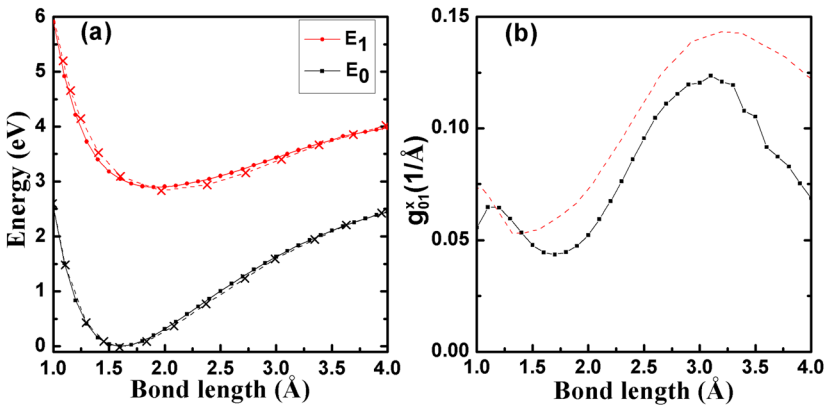

FIG. 1. (a) The energy of $1^1\sum^+$ (black curve) and $2^1\sum^+$ (red curve) states of LiH as a function of the bond length. The excitation energy computed with the present formulation (squares and dots) and with the previous formulation (crosses) using the AO basis set.[28] The energy minima of $1^1\sum^+$ are set to be zero. (b) NAC g^{x}_{01} between the two states as a function of the bond length. The NAC computed with the present formulation (black) and with the previous formulation (red) using the AO basis set.[28]

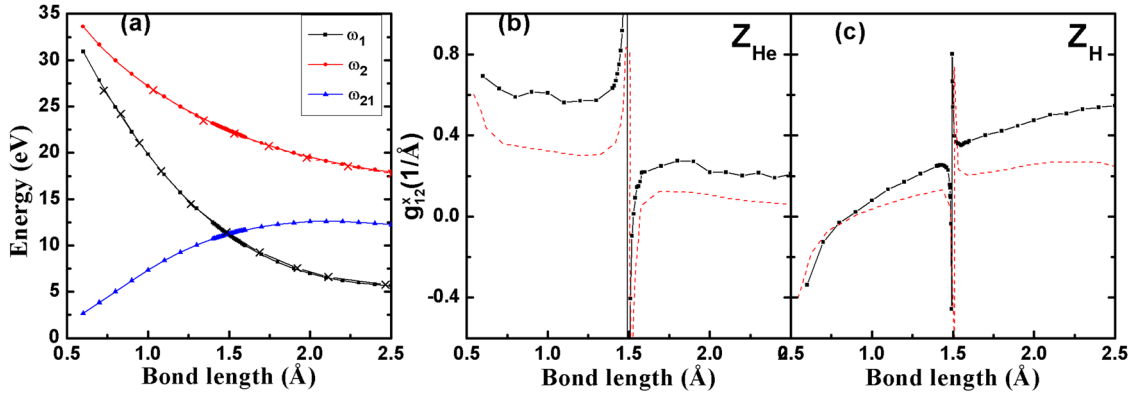

FIG. 2. (a) Excitation energies of the first two $^1\sum^+$ excited states ω_1 (black curve) and ω_2 (red curve) of HeH^+, as well as the energy difference between the two excited states ω_{21} (blue curve) as a function of the bond length. The excitation energy computed with the present formulation (squares and dots) and with the previous formulation (crosses) using the AO basis set.[28] The NAC between the two lowest $^1\sum^+$ excited states, g^x_{12}, with respect to the coordinates of (b) z_{He} and (c) z_H, as a function of the bond length. The z direction is along the bond direction of HeH^+. The NAC computed with the present formulation (black) and with the previous formulation (red) using the AO basis set.[28]

leads to an unphysical result shown below. In Figs. 2(b) and 2(c), we plot g^x_{12} with respect to the bond length in the z direction for the He atom and H atom, respectively, where the z direction is the bonding direction in HeH^+. In the case of HeH^+, the absolute values of g^x_{12} with respect to z_{He} and z_H are not the same. Again, the present results for g^x_{12} agree with the previous results using the AO (aug-cc-pVTZ) based NAC-TDDFT.[28] We find that g^x_{12} diverges near 1.5 Å, which is induced by the problematic solutions of $\tilde{\mathbf{T}}^{\pm}_{\alpha\beta}$ in Eq. (45) as alluded to earlier. The inverse of the super-matrix in Eq. (45) contains poles at $\pm\omega_\gamma - \omega_{\beta\alpha} = 0$. If the energy separation between the two excited states, $\omega_{\beta\alpha}$, approaches to the energy of one of them, ω_γ, Eq. (45) cannot be inverted and $\tilde{\mathbf{T}}^{\pm}_{\alpha\beta}$ diverges as $1/\left(\omega_\gamma - \omega_{\beta\alpha}\right)$. This is the reason for divergent g^x_{12} at the bond length of 1.5 Å, where ω_{21} curve intersects with the ω_1 curve as apparent in Fig. 2. This unphysical result is a consequence of an incorrect pole structure for the frequency-dependent quadratic response function in the adiabatic approximation, which is widely known.[27,29,53]

IV. CONCLUSIONS AND OUTLOOK

In summary, we have reformulated the first-order NAC in TDDFT with plane waves and PAW based on the linear and quadratic time-dependent response theory and hybrid exchange-correlation functionals. The Lagrangian functionals are employed to compute the NAC matrix elements in order to avoid the expensive derivative calculations of the KS orbitals with respect to ionic coordinates. The implemented methodology is validated for small molecules LiH and HeH^+, and the computed NAC matrix elements agree very well with the previous results using the AO basis.

One important extension of the formulation is to develop an accurate, efficient, and robust *ab initio* nonadiabatic molecular dynamics (NAMD) method for describing nonadiabatic excitations in molecular and extended systems. We are implementing the fewest-switches surface hopping (FSSH) algorithm[54–56] based on the proposed formulation. FSSH is one of the most popular NAMD methods, designed to minimize the number of stochastic hops. The execution of FSSH dynamics requires two key ingredients: (1) potential energy surface (PES) of excited states, including the excitation energy and ionic forces associated with the excited states. We have previously developed a TDDFT method which can compute the excitation energy and excited state forces based on plane waves and PAW[57] and (2) NAC between the excited states which can be computed based on the present formulation. To avoid the unphysical divergence of NAC in NAMD simulations, the pseudo-wavefunction approximation[25,27] can be employed to compute NAC when the energy difference between two excited states of interest coincides with the energy of another excited state. Under the pseudo-wavefunction approximation, the NAC is computed via Eq. (46) excluding $\tilde{T}^{\pm}_{i\sigma,\alpha\beta}$ terms.

For applications to large-scale systems, we could turn to approximations which can significantly reduce the computational costs while maintaining the similar accuracy. For example, we have developed an efficient TDDFT method[57] by projecting the complex TDKS matrix to a substantially reduced sub-Hilbert space. This method has proven to yield accurate excitation energy and ionic forces for large systems consisting of more than a thousand of atoms.[58,59] To reduce the computational cost of hybrid functionals, we can apply the first-order perturbation theory to the hybrid KS Hamiltonian which is not updated self-consistently.[60,61] Thus, the time-consuming Fock exchange integrals are calculated only once. This is somewhat analogous to the one-shot GW approximation. These two approximations can be applied when the exact formulation proposed in the present work becomes too expensive for certain problems.

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APPENDIX: EXPRESSION FOR TERMS IN EQ. (45) AND PARTIAL DERIVATIVES OF LAGRANGIAN

By the definition

$$\lim_{\omega_a\to\omega_\alpha,\omega_b\to-\omega_\beta}(\omega_\alpha-\omega_a)\left(\omega_\beta+\omega_b\right)\left|\tilde{V}^{\pm}_{i\sigma,ab}\right\rangle \equiv V^a_{0\alpha}V^b_{\beta 0}\left|\tilde{V}^{\pm}_{i\sigma,\alpha\beta}\right\rangle, \tag{A1}$$

the matrix elements of $\tilde{\mathbf{S}}\tilde{\mathbf{V}}^{\pm}_{\alpha\beta}$ are given by

$$\begin{aligned}
\tilde{S}\left|\tilde{V}^{\pm}_{i\sigma,\alpha\beta}\right\rangle = &\sum_{jk\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}_{k\tau}\right\rangle\left\{\left\langle\tilde{\psi}^{\mp}_{k\tau,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{\mp}_{j\tau,\beta}\right\rangle-\left\langle\tilde{\psi}^{\pm}_{k\tau,\beta}\middle|\tilde{S}\middle|\tilde{\psi}^{\pm}_{j\tau,\alpha}\right\rangle\right\}-\Bigg\{\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\pm}_{i\sigma,\alpha}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{\mp}_{j\tau,\beta}\right\rangle\\
&+\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\pm}_{i\sigma,\alpha}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\pm}_{j\tau,\beta}\tilde{\psi}_{j\tau}\right\rangle+\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\mp}_{i\sigma,\beta}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\pm}_{j\tau,\alpha}\right\rangle+\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}^{\mp}_{i\sigma,\beta}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\mp}_{j\tau,\alpha}\tilde{\psi}_{j\tau}\right\rangle\\
&+\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\mp}_{j\tau,\alpha}\tilde{\psi}^{\mp}_{j\tau,\beta}\right\rangle+\sum_{j\tau}\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\pm}_{j\tau,\beta}\tilde{\psi}^{\pm}_{j\tau,\alpha}\right\rangle\Bigg\}+\Bigg\{\sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\pm}_{j\sigma,\alpha}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{k\tau}\tilde{\psi}^{\mp}_{k\tau,\beta}\right\rangle\\
&+\sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\pm}_{j\sigma,\alpha}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\pm}_{k\tau,\beta}\tilde{\psi}_{k\tau}\right\rangle+\sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\mp}_{j\sigma,\beta}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{k\tau}\tilde{\psi}^{\pm}_{k\tau,\alpha}\right\rangle\\
&+\sum_{jk\tau}\tilde{S}\left|\tilde{\psi}^{\mp}_{j\sigma,\beta}\right\rangle\left\langle\tilde{\psi}_{j\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{\mp}_{k\tau,\alpha}\tilde{\psi}_{k\tau}\right\rangle\Bigg\}+\sum_{jj'\tau\tau'}\Big[\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}'_{\sigma\tau\tau'}\middle|\tilde{\psi}^{\mp}_{j\tau,\alpha}\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j'\tau',\beta}\tilde{\psi}_{j'\tau'}\right\rangle\\
&+\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}'_{\sigma\tau\tau'}\middle|\tilde{\psi}^{\mp}_{j\tau,\alpha}\tilde{\psi}_{j\tau}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\mp}_{j'\tau',\beta}\right\rangle+\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}'_{\sigma\tau\tau'}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\alpha}\tilde{\psi}^{\pm}_{j'\tau',\beta}\tilde{\psi}_{j'\tau'}\right\rangle+\left\langle\tilde{P}^{\sigma}_{c}\tilde{\psi}_{i\sigma}\middle|\tilde{K}'_{\sigma\tau\tau'}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{\pm}_{j\tau,\alpha}\tilde{\psi}_{j'\tau'}\tilde{\psi}^{\mp}_{j'\tau',\beta}\right\rangle\Big].
\end{aligned} \tag{A2}$$

The first term on the right-hand side of Eq. (51) is obtained by

$$\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\mathcal{T}^{\dagger}\frac{\partial}{\partial x}\mathcal{T}\middle|\tilde{\psi}_{i\sigma}\right\rangle=\sum_{IJ}\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{p}_I\right\rangle\left(\left\langle\phi_I\middle|\frac{\partial\phi_J}{\partial x}\right\rangle-\left\langle\tilde{\phi}_I\middle|\frac{\partial\tilde{\phi}_J}{\partial x}\right\rangle\right)\left\langle\tilde{p}_J|\tilde{\psi}_{i\sigma}\right\rangle+\sum_{IJ}\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{p}_I\right\rangle\left(\left\langle\phi_I\middle|\phi_J\right\rangle-\left\langle\tilde{\phi}_I\middle|\tilde{\phi}_J\right\rangle\right)\left\langle\frac{\partial\tilde{p}_J}{\partial x}\middle|\tilde{\psi}_{i\sigma}\right\rangle. \tag{A3}$$

The partial derivatives of KS Hamiltonian elements are expressed as

$$\begin{aligned}
\left\langle\tilde{\psi}_{i\sigma}\middle|\frac{\partial\tilde{H}^{\sigma}}{\partial x}\middle|\tilde{\psi}_{j\sigma}\right\rangle=&\int\left[\tilde{n}_{ij\sigma}(r)+\hat{n}_{ij\sigma}(r)\right]\frac{\partial v_{\mathrm{H}}[\tilde{n}_{\mathrm{Zc}}]}{\partial x}dr+\int\frac{\partial\hat{n}_{ij\sigma}(r)}{\partial x}\tilde{V}^{\sigma}_{\mathrm{loc}}(r)dr+\sum_{k\tau}\int\frac{\partial\hat{n}_{kk\tau}(r)}{\partial x}\Bigg\{\tilde{V}_{\mathrm{H}}\left[\tilde{n}_{ij\sigma}+\hat{n}_{ij\sigma}\right]\\
&+\frac{\delta^2E_{\mathrm{xc}}}{\delta n^{\sigma}\delta n^{\tau}}\left(\tilde{n}_{ij\sigma}+\hat{n}_{ij\sigma}\right)\Bigg\}dr+\sum_{k\tau,IJ,I'J'}\frac{\partial\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{k\tau}\right\rangle}{\partial x}\frac{\delta^2\left(E^1-\tilde{E}^1\right)}{\delta\rho^{\sigma}_{IJ}\delta\rho^{\tau}_{I'J'}}\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle\\
&+\sum_{IJ}\frac{\partial\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle}{\partial x}\left(D^1_{IJ}-\tilde{D}^1_{IJ}\right)-\sum_{k}\int\frac{\partial\hat{n}_{ik\sigma}(r)}{\partial x}\tilde{V}_{\mathrm{EX}}\left[\tilde{n}_{kj\sigma}+\hat{n}_{kj\sigma}\right]dr\\
&-\sum_{k}\int\frac{\partial\hat{n}_{kj\sigma}(r)}{\partial x}\tilde{V}_{\mathrm{EX}}[\tilde{n}_{ik\sigma}+\hat{n}_{ik\sigma}]dr-\sum_{(I,K)(J,L)}\left(K^1_{IJLK}-\tilde{K}^1_{IJLK}\right)\rho^{\sigma}_{LJ}\frac{\partial\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_K\middle|\tilde{\psi}_{j\sigma}\right\rangle}{\partial x}\\
&-\sum_{k,(I,K)(J,L)}\left(K^1_{IJLK}-\tilde{K}^1_{IJLK}\right)\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_K\middle|\tilde{\psi}_{j\sigma}\right\rangle\frac{\partial\left\langle\tilde{\psi}_{k\sigma}\middle|\tilde{p}_L\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{k\sigma}\right\rangle}{\partial x},
\end{aligned} \tag{A4}$$

where $v_{\mathrm{H}}[\tilde{n}_{\mathrm{Zc}}]$ represents the ionic pseudopotential due to the pseudo core charge density $\tilde{n}_{\mathrm{Zc}}$.

The partial derivative of $\mathcal{M}_{\alpha\beta}$ with respect to the ionic coordinate x is calculated by

$$\begin{aligned}\frac{\partial \mathcal{M}_{\alpha\beta}}{\partial x} &= \sum_{i\sigma}\left[\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\frac{\partial\left(\tilde{H}^{\sigma}-\varepsilon_{i\sigma}\tilde{S}\right)}{\partial x}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\frac{\partial\left(\tilde{H}^{\sigma}-\varepsilon_{i\sigma}\tilde{S}\right)}{\partial x}\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right]-\sum_{ij\sigma}\left\langle\tilde{\psi}_{i\sigma}\middle|\frac{\partial\tilde{H}^{\sigma}}{\partial x}\middle|\tilde{\psi}_{j\sigma}\right\rangle\left(\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{+}_{j\sigma,\beta}\right\rangle\right.\\&\left.+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\tilde{S}\middle|\tilde{\psi}^{-}_{j\sigma,\beta}\right\rangle\right)+\omega_{\beta}\sum_{i\sigma}\left(\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}^{+}_{i\sigma,\beta}\right\rangle-\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}^{-}_{i\sigma,\beta}\right\rangle\right)+\sum_{ij\sigma\tau}\frac{\partial}{\partial x}\left\{\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{+}_{j\tau,\beta}\right\rangle\right.\\&\left.+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{-}_{j\tau,\beta}\right\rangle+\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{-}_{j\tau,\beta}\tilde{\psi}_{j\tau}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{+}_{j\tau,\beta}\tilde{\psi}_{j\tau}\right\rangle\right\}\\&-\sum_{ijk\sigma\tau}\left\{\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}_{k\sigma}\right\rangle\left\langle\tilde{\psi}_{k\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{+}_{j\tau,\beta}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}_{k\sigma}\right\rangle\left\langle\tilde{\psi}_{k\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{j\tau}\tilde{\psi}^{-}_{j\tau,\beta}\right\rangle\right.\\&\left.+\left\langle\tilde{\psi}^{+}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}_{k\sigma}\right\rangle\left\langle\tilde{\psi}_{k\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{-}_{j\tau,\beta}\tilde{\psi}_{j\tau}\right\rangle+\left\langle\tilde{\psi}^{-}_{i\sigma,\alpha}\middle|\frac{\partial\tilde{S}}{\partial x}\middle|\tilde{\psi}_{k\sigma}\right\rangle\left\langle\tilde{\psi}_{k\sigma}\tilde{\psi}_{i\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}^{+}_{j\tau,\beta}\tilde{\psi}_{j\tau}\right\rangle\right\},\end{aligned}\tag{A5}$$

where the partial derivative of the kernel functional with respect to x is given by

$$\begin{aligned}&\frac{\partial\left\langle\tilde{\psi}_{i\sigma}\tilde{\psi}_{j\sigma}\middle|\tilde{K}_{\sigma\tau}\middle|\tilde{\psi}_{k\tau}\tilde{\psi}_{l\tau}\right\rangle}{\partial x}\\&=\int\frac{\partial\hat{n}_{ij\sigma}(r)}{\partial x}\left\{\tilde{V}_{\mathrm{H}}[\tilde{n}_{kl\tau}+\hat{n}_{kl\tau}]+\frac{\delta^2E_{\mathrm{xc}}}{\delta n^{\sigma}\delta n^{\tau}}(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})\right\}dr+\int\frac{\partial\hat{n}_{kl\tau}(r)}{\partial x}\left\{\tilde{V}_{\mathrm{H}}\left[\tilde{n}_{ij\sigma}+\hat{n}_{ij\sigma}\right]+\frac{\delta^2E_{\mathrm{xc}}}{\delta n^{\sigma}\delta n^{\tau}}\left(\tilde{n}_{ij\sigma}+\hat{n}_{ij\sigma}\right)\right\}dr\\&+\sum_{IJ,I'J'}\frac{\partial\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle}{\partial x}\frac{\delta^2\left(E^1-\tilde{E}^1\right)}{\delta\rho^{\sigma}_{IJ}\delta\rho^{\tau}_{I'J'}}\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{l\tau}\right\rangle+\sum_{IJ,I'J'}\frac{\partial\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{l\tau}\right\rangle}{\partial x}\frac{\delta^2\left(E^1-\tilde{E}^1\right)}{\delta\rho^{\sigma}_{IJ}\delta\rho^{\tau}_{I'J'}}\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle\\&+\sum_{m\tau'}\int\frac{\partial\hat{n}_{mm\tau'}(r)}{\partial x}\frac{\delta^3E_{\mathrm{xc}}}{\delta n^{\sigma}\delta n^{\tau}\delta n^{\tau'}}\left(\tilde{n}_{ij\sigma}+\hat{n}_{ij\sigma}\right)(\tilde{n}_{kl\tau}+\hat{n}_{kl\tau})dr+\sum_{m\tau',IJ,I'J',I''J''}\frac{\partial\left\langle\tilde{\psi}_{m\tau'}\middle|\tilde{p}_{I''}\right\rangle\left\langle\tilde{p}_{J''}\middle|\tilde{\psi}_{m\tau'}\right\rangle}{\partial x}\frac{\delta^3\left(E^1-\tilde{E}^1\right)}{\delta\rho^{\sigma}_{IJ}\delta\rho^{\tau}_{I'J'},\delta\rho^{\tau'}_{I''J''}}\\&\times\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{j\sigma}\right\rangle\left\langle\tilde{\psi}_{k\tau}\middle|\tilde{p}_{I'}\right\rangle\left\langle\tilde{p}_{J'}\middle|\tilde{\psi}_{l\tau}\right\rangle-\int\frac{\partial\hat{n}_{il\sigma}(r)}{\partial x}\tilde{V}_{\mathrm{EX}}\left[\tilde{n}_{kj\sigma}+\hat{n}_{kj\sigma}\right]dr-\int\frac{\partial\hat{n}_{kj\sigma}(r)}{\partial x}\tilde{V}_{\mathrm{EX}}[\tilde{n}_{il\sigma}+\hat{n}_{il\sigma}]dr\\&-\sum_{(I,K)(J,L)}\left(K^1_{IJLK}-\tilde{K}^1_{IJLK}\right)\frac{\partial\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_K\middle|\tilde{\psi}_{j\sigma}\right\rangle}{\partial x}\left\langle\tilde{\psi}_{k\sigma}\middle|\tilde{p}_L\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{l\sigma}\right\rangle\\&-\sum_{(I,K)(J,L)}\left(K^1_{IJLK}-\tilde{K}^1_{IJLK}\right)\left\langle\tilde{\psi}_{i\sigma}\middle|\tilde{p}_I\right\rangle\left\langle\tilde{p}_K\middle|\tilde{\psi}_{j\sigma}\right\rangle\frac{\partial\left\langle\tilde{\psi}_{k\sigma}\middle|\tilde{p}_L\right\rangle\left\langle\tilde{p}_J\middle|\tilde{\psi}_{l\sigma}\right\rangle}{\partial x}.\end{aligned}\tag{A6}$$

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